(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 220 941**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86308244.2

(22) Date of filing: 23.10.86

(51) Int. Cl.⁴: D 21 H 3/02, B 01 J 2/04

(30) Priority: 23.10.85 GB 8526158

(43) Date of publication of application: 06.05.87 Bulletin 87/19

(84) Designated Contracting States: AT BE CH DE ES FR GB IT LI LU NL SE

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(54) Paper sizing composition.

(57) Particulate solids comprising ketene dimers may be obtained by drying a conventional aqueous dispersion of the dimer to which a water dispersable encapsulating agent has been added. Preferably the encapsulating agent is a cationic starch and the solid is obtained by spray drying the emulsion under controlled conditions. The products retain their sizing properties even on prolonged storage.

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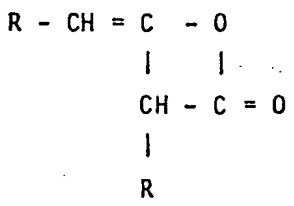
This invention relates to novel compositions comprising ketene dimers and to processes for their production.

Ketene dimers find use as ingredients of paper sizing compositions. The sizing compositions are manufactured in the form of relatively concentrated aqueous dispersions which are diluted before use in the paper sizing process. The concentrated aqueous dispersions suffer from the disadvantage that their efficiency as paper sizing agents deteriorates on prolonged storage apparently because of the hydrolysis of the ketene dimer. In order to be useful as paper sizes ketene dimers are dispersed in water in the presence of from 0.2 to 2.5% by weight of the weight of ketene dimer of a surfactant and/or an emulsifier. Attempts to dry such dispersions in the past have not been successful. If the dispersion is dried slowly the ketene dimer tends to hydrolyse. If the dispersion is dried at high temperatures the ketene dimer tends to char. If the dispersion is spray dried the material dries to a sticky mass which is difficult to handle.

We have now discovered a process for the manufacture of solid particulate compositions comprising ketene dimers and an encapsulating agent which are readily dispersible in water as is required in the paper sizing process and which exhibit improved stability upon prolonged storage. Solid compositions comprising solid particles of a ketene dimer and a water dispersable encapsulating agent are believed to be novel and constitute one aspect of this invention.

The ketene dimers which are useful as paper sizing agents are compounds having the molecular formula:



wherein R represents an alkyl, alkenyl, aryl or alkaryl group comprising from 8 to 24 carbon atoms. Preferably R represents an alkyl group having from 8 to 20 carbon atoms. These dimers are normally prepared from fatty acids obtained from natural sources and therefore comprise a mixture of dimers wherein the number of carbon atoms in the substituent group R varies. Mixtures of ketene dimers wherein R has an average value of from 8 to 24 are useful in the processes of this invention. Preferably the group R contains an average of from 12 to 18 and more preferably from 14 to 18 carbon atoms. Examples of ketene dimers include octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, tetracosyl, phenyl, benzyl, beta-napthyl and cyclohexyl keten dimers, as well as the ketene dimers prepared by known methods from montanic acid, naphthenic acid, ^{9,10}-decylenic acid, $^{9\text{-}10}$-dodecylenic acid, palmitoleic acid, oleic acid, ricinoleic acid, and eleostearic acid, as well as ketene dimers prepared from naturally occurring mixtures of fatty acids, such as those mixtures found in coconut oil, babassu oil, palm kernel oil, palm oil, olive oil, peanut oil, rape oil, beef tallow, lard (leaf) and whale blubber. Mixtures of any of the above-named fatty acids with each other may also be used.

The ketene dimers are manufactured in the form of waxy solids comprising the ketene dimers in admixture with up to 20% by weight of impurities. These products are normally used as such, i.e. without separation of the impurities. For the purposes of this disclosure all references to ketene dimers include mixtures thereof with these impurities and all proportions based on the weight of ketene dimer are based upon the weight of the manufactured product.

The encapsulating agent should be selected so as to be effective in enabling the dispersion to be dried to form a product which is redispersable in water and thereby useful in paper sizing processes. The nature of the encapsulating agent should be such that it is compatible with the other components of the spray dried product and such that it is not degraded during the drying process. Examples of compounds which may be useful as encapsulating agents are: gelatin, tristearin, gum arabic, sugars, ethyl cellulose,

carboxymethylcellulose, polyacrylamides, silicates, polyethers, polyesters, polyamides, starches especially cationic starches and polyvinyl alcohol.

The amount of encapsulating agent which is employed is proportional to the amount of ketene dimer in the dispersion and will normally be adjusted so as to be just sufficient to enable the dispersion to be dried. The use of excess quantities of encapsulating agent is less preferred. Normally the quantity of encapsulating agent which is added to the dispersion will be from 25 to 100%, preferably from 25 to 75% by weight of the weight of ketene dimer present in the dispersion. A preferred class of encapsulating agent are those which are known to be useful as ingredients of paper sizing compositions. Such agents may be employed in larger quantities than are required to sucessfully encapsulate the dimer since they make a contribution to the efficiency of the dried product used in the paper sizing process. Examples of such agents are starches such as cationic starches. A particularly preferred class of encapsulating agents are those which are known to disperse in cold water the preferred examples being certain cationic starches such as those sold under the Trade Marks Solvitose NX and Perfectamyl PLV. The encapsulating agent can be added to any aqueous dispersion of the ketene dimer. However it is strongly preferred to add the encapsulating agent to a dispersion which is itself useful as a paper size so that redispersion of the dried product produces a dispersion which is useful as a paper size without the need to disperse any additional components in order to form the size.

Ketene dimer dispersions normally comprise at least one surfactant and the presence of a surfactant in the dried product facilitates the redispersion of the product in the paper sizing process. Examples of suitable surfactants are the sodium salts of naphthalene formaldehyde sulphonate condensates, an ester of polyoxyethylene sorbitan or a sodium lignosulphonate.

The amount of surfactant added will usually be in the range 0.3 to 3.5% by weight of the ketene dimer, preferably in the range

1.25 to 2.5%.

The ketene dimer dispersions used in the spray drying processes may further comprise other conventional ingredients such as emulsifiers, stabilisers, retention aids and slimicides although the use of compounds which are sensitive to heat is preferably avoided.

In particular the ketene dimer dispersions preferably comprise a cationic polymer such as a polyamine in order to increase the efficiency of the dispersion as a paper size. Examples of polymers useful in this application water soluble polyamino polyamide-epichlohydrin resins, alkylene polyamine epichlorhydrin resins, poly (diallylamine)-epichlorhydrin resins, poly dialkyl dimethyl ammonium chloride and polyethyleneimines.

The amount of polymer present may be up to a weight ratio of ketene dimer to polymer of 1.0:1.0. However as the quantity of polymer increases there is an increasing tendency to produce a relatively sticky product and it is preferred that the weight ratio of ketene dimer to polymer is in the range 1.0:0.2 to 1.0:0.5.

The dispersion of the ketene dimer and the encapsulating agent can be dried by a variety of techniques. However exposure of the dimer to high temperatures for long periods can lead to its degradation either by charring or by hydrolysis and is best avoided. Techniques such as freeze drying and spray drying are preferably employed. We prefer to utilise spray drying although the conditions under which the drying is carried out must be monitored in order to minimise degradation of the ketene dimer. The spray drying of the ketene dimer dispersions can be carried out using conventional equipment. The temperature of the drier should be controlled so as to avoid any significant amount of charring or degradation of the components of the emulsion. Typically the temperature at the inlet to the dryer should be in the range 220° to 350°C and that at the outlet of the dryer 110° to 125°C. The drying process is carried out so as to produce a powdered product comprising less than 0.1% by weight of water.

The powder products must be dispersed in an aqueous medium in order to be useful in paper sizing processes. Typically the powder will be diluted with up to ten times its weight of water. Adequate dispersion is preferably obtained using vigorous agitation. We prefer to wet and/or slurry the powder with a small amount of water, e.g. about 5 to 30% by weight of the total dilution water is added to the powder, and to agitate those slurries with additional water to the desired content, usually about 10% by weight.

The invention is illustrated by the following examples:

Example 1

A dispersion of a stearic/palmitic alkyl ketene dimer having the following composition (Composition 1) was prepared.

	Water	800 Kgs
	Alkyl ketene dimer	100 Kgs
*	Orotan SN	1.24 Kgs
	a quaternised polyamine	100 Kgs
	Slimicide	400 mls

* the sodium salt of a napthalene formaldehyde sulphonate condensate.

A cationic starch product as sold under the Trade Mark Perfectamyl PLV was added to one sample of the dispersion in a quantity such that the ratio of the weight of ketene to starch was 1:1 (Composition 2). The same cationic starch product was added to a second sample of the dispersion in a quantity such that the ratio of the weight of ketene dimer to starch was 1:0.5 (Composition 3).

Compositions 2 and 3 were then spray dried using a Niro Production Minor Spray Drier set for Rotary Atomisation using an atomiser speed of 24,000 rpm. The liquor feed temperature was 15°C, the drier inlet temperature was 250°C and the drier outlet

temperature 125°C. The product was a white powder.

The sizing efficiency of these powders 2 and 3 and dispersion 1 was assessed in a series of trials.

Trial A

Composition	1 minute Cobb Value (gsm)	
	off drier 100 °C	Natural Cure
1	42.6	20.9
2	39.3	20.6
3	71.5	23.4

Sizing condition

Furnish	Brown Waste
Retention aid	0.02% solids/fibre
Size addition level	0.2% KD/Fibre

Trial B

Example	1 minute Cobb Value (gsm)	
	off drier 100 °C	Natural Cure
1	40.4	35.3
2	46.0	35.5
3	42.9	32.0

Sizing Conditions

Furnish	Bleached sulphite
Retention aid	0.02% solids/fibre
Size addition level	0.1% KD/Fibre

Trial C

Example	1 minute Cobb Value (gsm) off drier 100 °C	Natural Cure
1	69.2	38.8
2	37.8	25.0
3	32.2	25.5

Sizing Conditions

Furnish	Brown waste
Retention aid	0.02% solids/fibre
Size addition level	0.2% KD/Fibre

Trial D

Example	1 minute Cobb Value (gsm) off drier 100 °C	Natural Cure
1	127.7	117.9
2	96.4	102.9
3	103.6	96.6

Sizing Conditions

Furnish	Bleached sulphite
Retention aid	0.02% solids/fibre
Size addition level	0.1% KD/Fibre

Trial E

Example	1 minute Cobb Value (gsm) off drier 100 °C	Natural Cure
1	86.3	40.5
2	118.9	33.5
3	120.5	38.1

Sizing Conditions

Furnish	Brown waste
Retention aid	0.02% solids/fibre
Size addition level	0.2% KD/Fibre

Trial F

Example	1 minute Cobb Value (gsm) off drier 100 °C	Natural Cure
1	90.7	81.7
2	32.6	25.3
3	30.3	26.7

Sizing Conditions

Furnish	Bleached sulphite
Retention aid	0.02% solids/fibre
Size addition level	0.2% KD/Fibre

Trials G and H are based on a product (Composition 4) with a surfactant content on ketene dimer of 0.62% but which are otherwise identical with and are manufactured under the same conditions as composition 3 described above.

Trial G

Example	1 minute Cobb Value (gsm)	
	off drier 100 °C	Natural Cure
1	32.0	25.8
4	43.9	28.9

Sizing Conditions

Furnish	Bleached sulphite + 5% chalk
Retention aid	0.02% solids/fibre
Size addition level	0.1% KD/Fibre

Trial H

Example	1 minute Cobb Value (gsm)	
	off drier 100 °C	Natural Cure
1	36.0	23.3
4	34.5	25.0

Furnish	Brown waste
Retention aid	0.02% solids/fibre
Size addition level	0.2% KD/Fibre

Trial J is based on a product (Composition 5) with a surfactant content on ketene dimer of 2.8% but which is otherwise identical with and is manufactured under the same conditions as composition 3.

Trial J

Example	1 minute Cobb Value (gsm)	
	off drier 100 °C	Natural Cure
1	37.6	27.8
5	44.6	32.6

Size conditions

Furnish	Bleached sulphite + 10% chalk
Retention aid	0.02% solids/fibre
Size addition level	0.5% KD/Fibre

Example 2

A dispersion (composition 6) of a stearic/palmitic alkyl ketene dimer having the following composition was prepared:-

Alkyl ketene dimer	100 kgs
Orotan SN	0.62 kgs
Quaternised Polyamine	50 kgs
Slimicide	400 mls
Water	850 kgs

A cationic starch product as sold under the Trade mark Solvitose NX was added to this dispersion in a quantity such that the ratio of the weight of ketene dimer to starch was 1:0.5 (composition 7).

Composition 7 was then spray dried using the conditions set forth in Example 1. The efficiency of sizing of compositions 6 and 7 was then assessed at that time and after storage at ambient temperatures for 3.5 and 4.5 months. The results were as follows:-

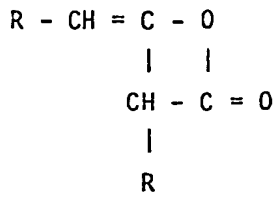
Composition	1 minute cobb value (gsm)	
	off drier 100 °C	Natural Cure
6	28.2	24.2
7	31.6	25.4
after 3½ months		
6	26.2	27.0
7	33.6	26.5
after 4½ months		
6	62.6	40.8
7	33.6	26.5

Sizing conditions

Furnish	Bleached sulphite
Retention Aid	0.02 solids/fibre
Size Addition	0.1 KD/fibre

Claims

1. A particulate solid composition comprising ketene dimer of the formula:



wherein R represents an alkyl, alkenyl aryl or alkaryl group having from 8 to 24 carbon atoms and a water dispersable encapsulating agent.

2. A composition according to claim 1 characterised in that R represents an alkyl group comprising from 12 to 18 carbon atoms.

3. A composition according to claim 2 characterised in that R represents an alkyl group comprising from 14 to 18 carbon atoms.

4. A composition according to any of the preceeding claims characterised in that the encapsulating agent is a cationic starch.

5. A composition according to any of the preceding claims characterised in that the ratio of the weight of ketene dimer to the weight of encapsulating agent is in the range 1:0.25 to 1:1.

6. A composition according to claim 5 characterised in that the weight of the ratio is in the range 1:0.25 to 1:0.75.

7. A composition according to any of the preceding claims characterised in that the particles comprise a polymeric cationic dispersing agent.

8. A composition according to claim 7 characterised in that the dispersing agent is selected from the group comprising water-soluble

polyaminepolyamide epichlorhydrin resins, alkylene polyamine epichlorhydrin resins and poly (diallylamine)-epichlorhydrin resins.

9. A composition according to either of claims 7 or 8 characterised in that the ratio of the weight of ketene dimer to the weight of dispersing agent is in the range 1:0.5 to 1:1.

10. A composition according to any of the preceding claims charaterised in that the particles comprise at least one surfactant.

11. A composition according to claim 10 characterised in that the surfactant is selected from the group comprising the salts of napthalene formaldhyde sulphonate condensates, esters of polyoxyethylene sorbitan and salts of lignosulphonic acids.

12. A composition according to either of claim 10 or 11 characterised in that the weight of surfactant present is from 0.3 to 3.5% of the weight of ketene dimer.

13. A process for the production of a composition according to any of claims 1 to 12 wherein the components of the composition are formulated into an aqueous dispersion and that dispersion is dried.

14. A process according to claim 13 characterised in that the dispersion is dried by passage through a spray drier.

15. A process according to claim 14 characterised in that the temperature inlet to the drier is in the range 220 to 350°C and the temperature at the outlet to the drier is in the range 110° to 125°C.

16. A process for the production of sized paper or paper board wherein a sizing agent is added to the paper or paper stock characterised in that the sizing agent comprises an aqueous dispersion of a particulate solid according to any of claims 1 to 12 or which has been produced by a process according to any of claims 13 to 15.

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European Patent Office

Application number

EP 86 30 8244

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	RESEARCH DISCLOSURE, no. 203, March 1981, pages 132,133, disclosure no. 20336, Industrial Opportunities Ltd, Hampshire, GB; S. A. COLBY et al.: "Method for making paper with polymer-encapsulated sizing agent" * Page 132 *	1-3,5 8,16	D 21 H 3/02 B 01 J 2/04
X	US-A-3 311 532 (R. J. KULICK et al.) * Claims 1,5-8,12,13; examples 6,9,11,12 *	1-12, 16	
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 53, no. 11, May 1983, page 1323, abstract no. 12331, Appleton, Wisconsin, US; & JP-A-112 498/82 (KAO SOAP CO.) 13-07-1982 * The whole abstract *	1-3,5, 6,10, 16	TECHNICAL FIELDS SEARCHED (Int. Cl.4) D 21 H
A	US-A-4 296 012 (T. OKUMICHI et al.) * Claims 1-4,6,7; column 3, line 15 - column 5, line 55; example 1 *	1-3,5-12,16	

-/-

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22-01-1987	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Application number

EP 86 30 8244

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-3 637 407 (U. SCHOBINGER et al.) * Claims 1,2,5,10-14,16,17; example B *	1-3,5 10,16	
A	US-A-3 223 544 (A. R. SAVINA) * Whole document *	4,10-12	
A	US-A-2 901 371 (H. G. ARLT, Jr.) * Whole document *	1-3,16	
A	US-A-2 865 743 (C. A. WEISGERBER) * Claims 1,2,5-9,11; column 4, line 43 - column 5, line 44 *	1-3,13 -16	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	DE-B-1 176 993 (BATTELLE-INSTITUT) * Claim; column 3, lines 8-18; example 2 *	14	
A	GB-A-1 405 751 (BPB INDUSTRIES) * Claims 1,6; examples 1,2 *	13-15	

The present search report has been drawn up for all claims

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THE HAGUE	22-01-1987	NESTBY K.

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D : document cited in the application
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